Science of the Total Environment 463–464 (2013) 1049–1059

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Processes and impacts of acid discharges on a natural substratum under a landfill

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HIGHLIGHTS

- Acidity decreased the ability of a substratum to retain leachate pollutants, which travelled further than one-meter depth.
- Acidity affects a clay-sand substratum and its impact prevails despite the presence of a methanogenic leachate.
- These effects are minerals dissolution, decrease of density and CEC, increase of hydraulic conductivity, metals release.
- Acidity also causes elimination of neutralizing capacity and formation of low-CEC-clays (kaolinite).
- Landfills should avoid acid deposits (or otherwise add lime) and be placed on illitic substrata better than kaolinitic ones.

ARTICLE INFO

Article history:
Received 17 January 2013
Received in revised form 21 May 2013
Accepted 2 June 2013
Available online 24 July 2013

Editor: Simon James Pollard

Keywords:
Landfill pollution
Acidity impact
Cation exchange
Kaolinite–illite materials

ABSTRACT

Analyses of substratum samples under a landfill were performed to assess the pollution impact of waste over a clay–sand material after nine years of exposure. These samples presented different illite/kaolinite ratios and an acid pH, especially low near the waste/soil contact in a 1–1.5 m soil thickness with low density and despite the basic pH of the collected actual methanogenic leachate. This study has raised the effects of a presumably acid stage in the waste leachate on the substratum final quality of clay and its physical–chemical properties as an attenuation buffer. These effects were the dissolution of carbonate minerals, decrease of dry density, increase of hydraulic conductivity, release of metals and formation of clays with low cationic exchange capacity (CEC) as kaolinite. The large presence of H^+ and $Al(OH)_3^{x+}{}_x$ depleted the neutralizing capacity of the substratum and occupied exchangeable sites, decreasing therefore the available sites for retaining leachate pollutants, which traveled further than the first-meter depth of the substratum. In order to combat and prevent pollution as well as to preserve the good barrier properties under new landfills it is proposed to select illitic materials better than kaolinitic substratum, to avoid acid landfilling and if not possible to add lime.

1. Introduction

The large quantity of municipal waste (MW) that is produced (more than 520 kg pc^{-1} $year^{-1}$ in EU-27 (Eurostat Data Centre on Waste, 2010)) and the estimated growth rate of 2% $year^{-1}$ (EEA, 2007), jeopardize the sustainability of natural systems, which are unable to absorb waste impacts (WCED, 1987). The disposal in landfills is the oldest and most used waste treatment in the world (Williams, 2005) and generates a polluting leachate that can migrate through the soil and damage surface water and groundwater and, therefore, the living beings in contact with these systems (Chan et al., 1997; Sanchez-Chardi and Nadal, 2007; Unnisa et al., 2008; Baran et al., 2009; Goorah et al., 2009; Barcic and Ivancic, 2010).

Although since the 1990s landfills are subjected to strict security measures, which include artificial sealing liners; the number of landfills without safe barriers still remains high in low income countries (Sharholy et al., 2008) and also in developed countries where old landfills previous to the legislation are abundant (150,000 of closed and abandoned old landfills in Europe (SUFALNET4EU-PROJECT (2005)). Furthermore, even the liners, caps and leachate collection systems of new landfills are likely to fail (Elsbury and Sraders, 1989; Rollin et al., 1991; Potter and Yong, 1993; Rodic and Goossens, 1993; Suter et al., 1993; Christensen et al., 1994; Rowe, 1994; Averesch, 1995; Buss et al., 1995; Surmann et al., 1995); in some

Abbreviations: B1, borehole 1; B2, borehole 2; BOD, biological oxygen demand; $Cation^{x+}{}_{sol}$, soluble cation; $Cation^{x+}{}_{ex}$, exchangeable cation; CEC, cationic exchange capacity; COD, chemical oxygen demand; δ, dry density; EC, electrical conductivity; Eh, redox potential; h, moisture; MW, municipal waste; pc, per capita; SSA, specific surface area (external); TA, total alkalinity; TAC, total alkalinity of carbonates; WSOC, water soluble organic carbon.

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http://dx.doi.org/10.1016/j.scitotenv.2013.06.047

cases in less than 10 years (Rowe and Sangam, 2002), depending on the material and exposure conditions. For these reasons, a predictable response of the substratum to leachate is a preventive measure for minimizing the impacts of waste deposits in both old and new landfills. In addition, to predict the behavior of the leachate in the event of sealing failure through the mineral substratum, is one of the independent consecutive liners integrated in the multibarrier concept (Bilitewski et al., 1997).

Demonstrating the safety of landfills as long as the waste persists is worth to be evaluated, as there the waste is not recovered, but deposited on a permanent basis. The main objectives here are to follow the spatial variation of the main components of the pollution front and to detect possible processes and alterations in the underlying material in contact with the leachate. For this purpose, a 9-year old landfill without initial implementation of safety engineered barriers was studied to observe the potential hazards of leachate extent through the substratum and, when possible, to propose prevention techniques in order to protect human health, natural resources and the environment.

At present there are few studies that analyzed soil samples in real landfills, if any, they did not collect samples at different depths, or examined the leachate and the number of samples or parameters measured were much smaller than in the present study (King et al., 1993; Frascari et al., 2004). In this respect, the composition of the exchange complex, the NH_4^+ content or the soil pH are especially missing. To date, only three materials underlying landfills from the South-West of Europe (Regadío et al., 2012) have been extensively examined both for their physical–chemical properties and for their soil characteristics. The actual paper is complementary to that one in the way both analyze substrata samples collected at different vertical distances beneath the waste (i.e., the pollution source). In the case described earlier, the three landfills were built on clay-rich substrata, mostly of smectite–illite type, where neutral to slightly basic conditions prevailed. In this case, the mineralogy is different and the origin of the detected acidity condition of the clay substratum is discussed.

Table 1
Dates of the borehole performances, waste thicknesses, sample thicknesses and average depths of the samples.

Borehole 1 (B1)			Borehole 2 (B2)		
mm/dd/yy	Waste thickness (m)		mm/dd/yy	Waste thickness (m)	
07/01/08	7.8		07/02/08	9.8	
Sample	Thicknesses (10^{-2} m)	Depths[a] (m)	Sample	Thicknesses (10^{-2} m)	Depths[a] (m)
S01	2.5	0.01	S01	2.5	0.01
S02	2.5	0.04	S02	2.5	0.04
S03	2.5	0.06	S03	2.5	0.06
S04	2.5	0.09	S04	2.5	0.09
S05	5.0	0.13	S05	5.0	0.13
S06	5.0	0.23	S06	5.0	0.18
S07	10.0	0.30	S07	10.0	0.25
S08	5.0	0.38	S08	5.0	0.33
S09	20.0	0.50	S09	10.0	0.95
S10	10.0	1.10	S10	13.0	1.07
S11	10.0	1.25	S11	9.4	1.20
S12	10.0	1.35	S12	8.0	2.52
S13	10.0	1.65	S13	12.0	3.63
S14	10.0	2.05			
S15	10.0	2.35			

[a] Average depth measured from the waste bottom.

2. Materials and methods

2.1. Materials

Substratum samples were taken under a landfill without engineered liners, placed in Cantabria, Northern Spain (Fig. 1.a). The landfill (nine years of age) had an area of 10 ha and received 410,000 t $year^{-1}$ of municipal debris and non-hazardous industrial waste according to local administration. The landfill is situated in a forestry land, over detritic deposits of silt, clay and sandstones from the Lower Cretaceous period. A hole from a former quarry served to form the landfill body. The slopes are moderate, decreasing from the South-East to the North-West.

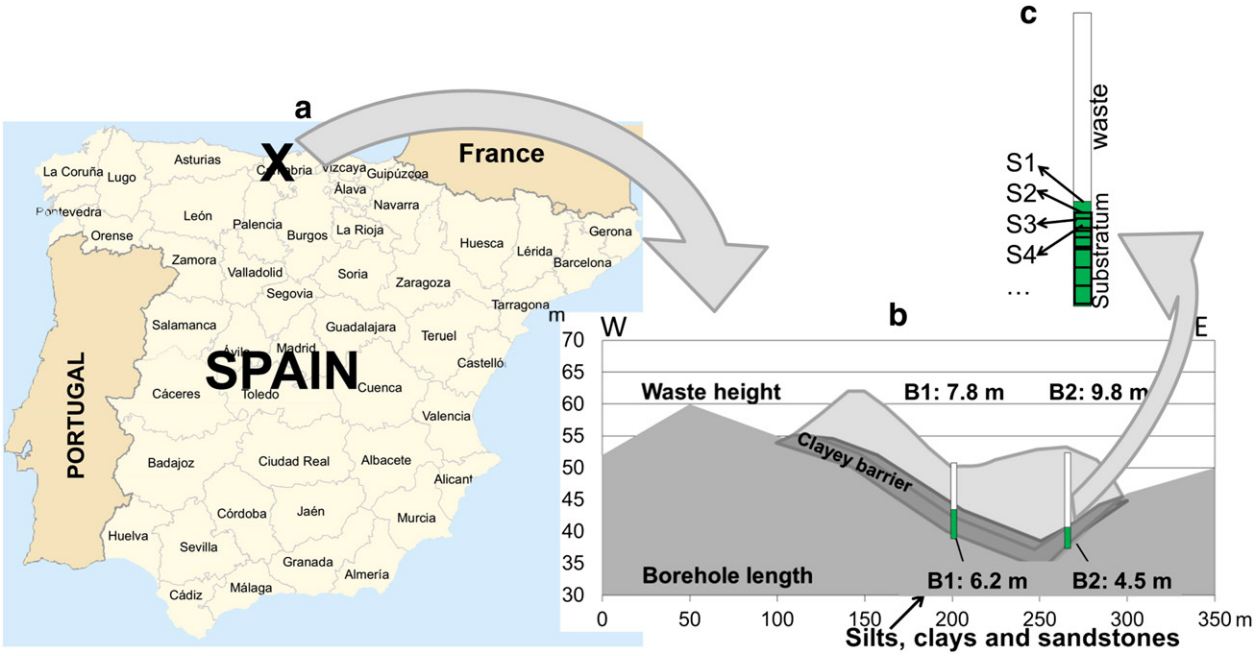


Fig. 1. a) Location of the landfill (Spain). b) Cross section of the landfill that represents the waste, the boreholes (lengths of pierced waste and recovered cores) and the underlying substratum. c) Schematic drawing of the sampling.

The region had an Atlantic climate, with an annual average temperature of 13.8 °C (the monthly maximum and minimum are 19.4 °C in July and 8.9 °C in January, respectively) and an annual average rainfall of 1326 mm (the monthly maximum and minimum are 157 mm in November and 49 mm in July, respectively).

Two boreholes (B1 and B2) about 65 m apart were performed by rotational drills in the North sector and on each side of a small valley (Fig. 1.b). The boreholes passed through the waste (which was discarded) and extracted the corresponding cores from the first 2 to 4 m of the natural substratum. These cores were divided into 28 samples of different thicknesses and at different depths by cutting cross-sections (Fig. 1.c and Table 1). Finally, the samples were homogenized, preserved dark and refrigerated (4 °C) until their analyses.

2.2. Analytical methods

Several physical, chemical and mineralogical parameters were measured in the soil substratum as a function of depth. pH, redox potential (Eh) and electrical conductivity (EC) were analyzed in aqueous extracts (1:2.5 soil:de-ionized water ratio) at laboratory temperature and in duplicate following official methods (Ministerio de Agricultura, 1994).The dry density (δ) was calculated following Eq. (1), after estimating the water saturated density (δ_b) by the hydrostatic balance method (McIntyre and Loveday, 1974) and Eq. (2).

$$\delta = \delta_b/(1 + h_r) \quad (1)$$

where h_r = moisture (ratio).

$$\delta_b = m_a/\left(m_{ap} - m_{wp}\right) \quad (2)$$

where:

m_a mass of an unaltered portion of the sample
m_{ap} mass of the sample portion with a paraffin cover measured in the air
m_{wp} mass of the sample portion with a paraffin cover measured submerged in water.

The percentage of water content or moisture (h) was calculated in duplicate to refer liquid extract data to dry solid sample mass (Eq. (3)). A portion of non-altered sample was weighed (m_m) and the same fraction was weighed again (m_d) after being at 105 °C for 48 h.

$$h = (m_m - m_d)/m_d \cdot 100 \quad (3)$$

The remained portions, dried at 105 °C, were mechanically grinded by Retsch MM200 microball mill, at 20 s^{-1} frequency for 5 min to obtain a homogeneous particle size (<5 μm) for global mineralogy and external specific surface analyses (Brunauer, Emmett and Teller (BET) method, e.g., Webb and Orr (1997)). The mineralogy was performed in two parts: (i) the random powder method (Bish and Reynolds, 1997) to estimate the overall mineralogical composition from all samples and (ii) the oriented slide method (Moore and Reynolds, 1997) to determine the specific families of clay minerals (sheet silicates) from some pre-selected samples (Table 2). In the second case, the samples were pre-selected according to the proximity to the waste and to mineralogical variations detected in the random powder analysis. Mineralogy results are presented in mass percentages out of the total mass of minerals in the sample and in terms of means ± standard deviations.

The diffractometer was an X-ray Philips X'Pert with a Ni-filtered radiation of CuK α (λ = 0.15406 nm) and an X-CELERATOR detector. Samples were registered at a tension and a current of 40 kV and 40 mA, with 0.016° $step^{-1}$ with an equivalent time of 100 s $step^{-1}$. The software used for data analysis was DRXWIN® (Primo, 2001).

With regard to the external surface analysis, about 0.20 g of grinded sample was degassed with N_2 during 18 h at 90 °C (UNE 22-164-94 (1994)) using a Flow-Prep 060 station Micromeritics™. Then, the external specific surface area (SSA) was measured by the BET method of adsorption isotherms of nitrogen gas at 77 K with Micromeritics® GEMINI V, using an analysis protocol software which obtains a five-point N_2 adsorption isotherm.

The exchangeable cations (Na^+_{ex}, K^+_{ex}, Ca^{2+}_{ex}, Mg^{2+}_{ex}, $NH_4^+{}_{ex}$) were extracted from 10 g of the original not-dried samples (i.e., without 105 °C drying) in 100 mL of de-ionized water, at room temperature as described by Thomas (1982). The soluble ions (Na^+_{sol}, K^+_{sol}, Ca^{2+}_{sol}, Mg^{2+}_{sol}, $NH_4^+{}_{sol}$, alkalinity) were analyzed in two replicates of aqueous extracts (1:10 soil:de-ionized water) also from the original refrigerated samples. Na^+ and K^+ were determined using a Buck Scientific® PFP-7 flame photometer. Ca^{2+} and Mg^{2+} were analyzed by Flame Atomic Absorption Spectroscopy (Unicam™ Solaar M series atomic absorption spectrometer). NH_4^+ was determined using an ion selective potentiometer (ORION® 9512 Ammonia Gas Sensing Electrode). Alkalinity was analyzed with ORION® 960 potentiometer by titration using normalized H_2SO_4 solution as the titrant and a pH-meter to obtain the titration curve. Furthermore, the cationic exchange capacity (CEC) was determined as described in Rhoades (1982), measuring the final Na^+ concentration (equivalent to the CEC) in the previously mentioned flame photometer.

All liquid extracts were done with wet sample to avoid any alteration of the original conditions in order not to modify neither alkalinity nor aqueous NH_4^+ by a previous heating treatment. Water content in the used wet sample was calculated and used to express the obtained results from the analyses of these liquid extracts as a function of dry mass of solid.

Finally, thin sections (30-μm thickness) of previously freeze dried slides from shallow and unaltered substratum materials were prepared. The method (Cobeña et al., 1999) uses LR White resin Standard (ref. 62661-500ML-F) to indurate the material and to observe its textural qualities with a petrographic optical microscope (Ortho Plan Pol Leitz Carl Zeiss).

Table 2
Information about the XRD analysis.

	Overall mineralogy	Sheet silicate mineralogy
Method	Random powder	Oriented slide
Initial sample conditions	Dried at 105 °C, grinded and mixed with ZnO (Srodon et al., 2001)	<2 μm size fraction extracted from the original-refrigerated non-altered samples
Intensity limits	Between 3 and 70 2°θ	Between 3 and 20 2°θ
Reflective powers for the semi-quantification of minerals	Schultz (1964)	UNE 22-164-94 (1994) and Barahona (1974)

3. Results

3.1. Leachate

An actual leachate sample was collected from an existing drainage well. The leachate analysis (Table 3) shows that it is a sodium chloride-aqueous solution. The leachate presents a relatively small EC and a pH more basic compared to most other studied leachates (Table 6 in Regadío et al. (2012:493)). Accordingly, the soluble salt contents (e.g., Cl^- and NH_4^+) and the organic components (biological oxygen demand, BOD; and chemical oxygen demand, COD) are also lower than the average for municipal landfill leachate. The most abundant anions are those concerning the alkalinity and the Cl^-, followed, but to a much lesser amount, by SO_4^{2-} and NO_2^-. The most

Table 3
Chemical analysis of the Cantabria landfill leachate.

Parameters		mg L^{-1}
pH		7.70
EC (mS m^{-1})		780
O_2		0.48
COD		430
BOD		894
BOD/COD		2.08
Cl^-		817
SO_4^{2-}		11
F^-		1
NO_2^-		11
Alkalinity	TA–TAC	410
	TAC	480
NH_4^+		280
Ca^{2+}		185
Mg^{2+}		175
K^+		270
Na^+		820
Fe		0.21
WSOC		351
Phenols		0.047
Benzene		<0.50
Toluene		215
Ethylbenzene		1.80
Xylenes		6.90
Cr		0.04
Pb		<0.10
Zn		<0.02
Cd		<0.02

COD: chemical oxygen demand, BOD: biological oxygen demand, TA: total alkalinity, TAC: total alkalinity of carbonates (mostly HCO_3^- for the given pH), WSOC: water soluble organic carbon.

common cation (Na^+) is followed by concentrations still noticeable of $NH_4^+ \approx K^+ > Ca^{2+} \approx Mg^{2+}$. Finally, the low dissolved O_2 content indicates anaerobic conditions.

The visible amount of NO_2^- and Fe^{2+}, as well as the predominance of organic carbon (WSOC) over inorganic carbon, is typical of an actual reduction environment in the actual leachate–substratum interface.

As this is a one-off measure, it cannot be used as a permanent value, because leachate composition varies with location, landfill age (i.e., degree of waste stabilization), landfill technology, climate and waste composition (Chian and DeWalle, 1976; Vadillo et al., 1999; Christensen et al., 2001; Renou et al., 2008). Nevertheless, it helps to have an idea of the leachate composition at the moment, reducing uncertainty.

Trace element species (<1 mg L^{-1}), phenols and BTEX compounds were not analyzed in the soil substratum samples.

3.2. Soil properties: substratum samples

The substratum is a clayey material (32 ± 12 mass % of sheet silicates), composed of kaolinite (17 ± 8%) and illite (16 ± 9%), without any associated minerals other than the everywhere-present quartz (65 ± 11 mass %) and feldspars (3 ± 1 mass %). Carbonate minerals are punctually found as limestone clasts of $0.33 \cdot 10^{-3}$ m diameter (Fig. 2.a), coming probably from building materials buried in the landfill. Nevertheless, most of the landfill substratum is a quartz artificial micro-conglomerate with a brown-red mixture of clay and iron oxide matrix (Fig. 2.b).

The mass percentage of sheet silicates, the SSA (10 ± 5 $m^2\ g^{-1}$) and the CEC (7.1 ± 3.3 $cmol^+\ kg^{-1}$) follow a similar pattern with depth (Fig. 3). These three parameters have a noticeable variability: sheet silicates fluctuate from 7 to 68%, the SSA varies from 1.55 to 19.50 $m^2\ g^{-1}$ and the CEC from 0.5 to 14.4 $cmol^+\ kg^{-1}$. The sheet silicates and the SSA are higher in samples from B1 than from B2, while the opposite is true for the CEC. The exchange complex is dominated by Ca^{2+} and Mg^{2+}, with a ratio Ca^{2+}/Mg^{2+}, much bigger in B2 than in B1. The sum of the exchangeable cations is lower than the measured CEC in B1, while in B2 the total of the exchangeable cations, dominated by Ca^{2+}_{ex}, exceeds the CEC (Table 4).

The pH is generally acid in both boreholes (5.9 ± 1.2), especially throughout the entire B1 and along the first 1.25 m of B2; being in all cases B1 more acidic than B2 (Table 5). The Eh (113–350 mV) is higher in B1 (268 ± 40 mV) than in B2 (171 ± 29 mV), while the EC (quite low in general) and h (9.55–43.35%), are smaller in B1 (12 ± 6 mS m^{-1} and 17.98 ± 3.36%) than in B2 (47 ± 58 mS m^{-1} and 25.42 ± 10.78%) (Table 6).

The substratum presents high dry density (δ) with an important variability: (1.65–2.04) · 10^3 kg m^{-3} in B1 and (1.28–2.04) · 10^3 kg m^{-3} in B2 (Fig. 4). The lowest values are measured in a shallow layer. This layer is presumably made up of removed materials of heterogeneous and unconsolidated nature which were probably deposited to fill the gap of the abandoned quarry. The highest densities are at 2 m and 1.25 m for the respective boreholes, remaining constant from those depths down.

3.3. Leachate infiltration

Dissolved salts of the substratum samples have been measured to follow the leachate effect. Low concentrations of inorganic ions were quantified in both boreholes (Table 6), even those most abundant in the leachate (Na^+, NH_4^+, K^+). Cl^- is present in low quantities with an average of 0.6 ± 0.5 mmol kg^{-1}, ranging from 0 up to 1.35 mmol kg^{-1}. No presence of SO_4^{2-} is measured in the samples. Alkalinity (HCO_3^-) was not detected in any sample of B1 (due to the acidic conditions found in the entire profile), while in B2 was generally the major species, although in small concentrations. Water soluble organic carbon (WSOC) is present in relatively low concentrations too, higher in B1 (163 ± 141 μg g^{-1}) than in B2 (134 ±42 μg g^{-1}). The maxima values of WSOC are in shallower samples (218 ± 142 μg g^{-1} up to 1.1 m and 153 ± 30 μg g^{-1} up to 0.95 m in B1 and B2, respectively) than the minima values (53 ± 31 μg g^{-1} from 1.1 m down and 91 ± 33 μg g^{-1} from 0.95 m down in B1and B2, respectively).

No tendency with depth was recognized in B1 for most of the soluble ions, with the exception of the ammonium and organic compound attenuations. In contrast B2 showed general decrease of the ion concentration with depth, contrary to the observed increase of pH with depth. Alkalinity, soluble and exchangeable cations of B2 have the highest concentrations at shallow samples which drop 86–97% from 1.2 m-depth and below.

4. Discussion

4.1. Leachate

Atlantic weather has little variance between the maximum and minimum values of rainfall and temperature and therefore the measurements from the leachate are expected to be reproducible throughout the year, as the precipitation and temperature patterns are more homogeneously distributed than Mediterranean climate (Tatsi and Zouboulis, 2002). The relatively low organic and inorganic salt content in the landfill leachate (Table 3) may be due to the Atlantic climate which is characterized by high precipitations and low monthly maxima temperatures. This causes a greater quantity of leachate that is very diluted and contributes to the hastening of the waste stabilization to an inert state, as water catalyzes these degradation reactions. For both reasons, the main ion concentrations are lowered in mature leachates. Furthermore, Ca^{2+}, Mg^{2+}, Fe^{2+} and Mn^{2+} decrease in methanogenesis because the increase of both pH and CO_2 makes them to precipitate as hydroxides or carbonates.

The organic acid anions are released in large quantities during the acetogenesis but, in the methanogenic stage, they are consumed in redox reactions. The concentration of organic acid anions (represented

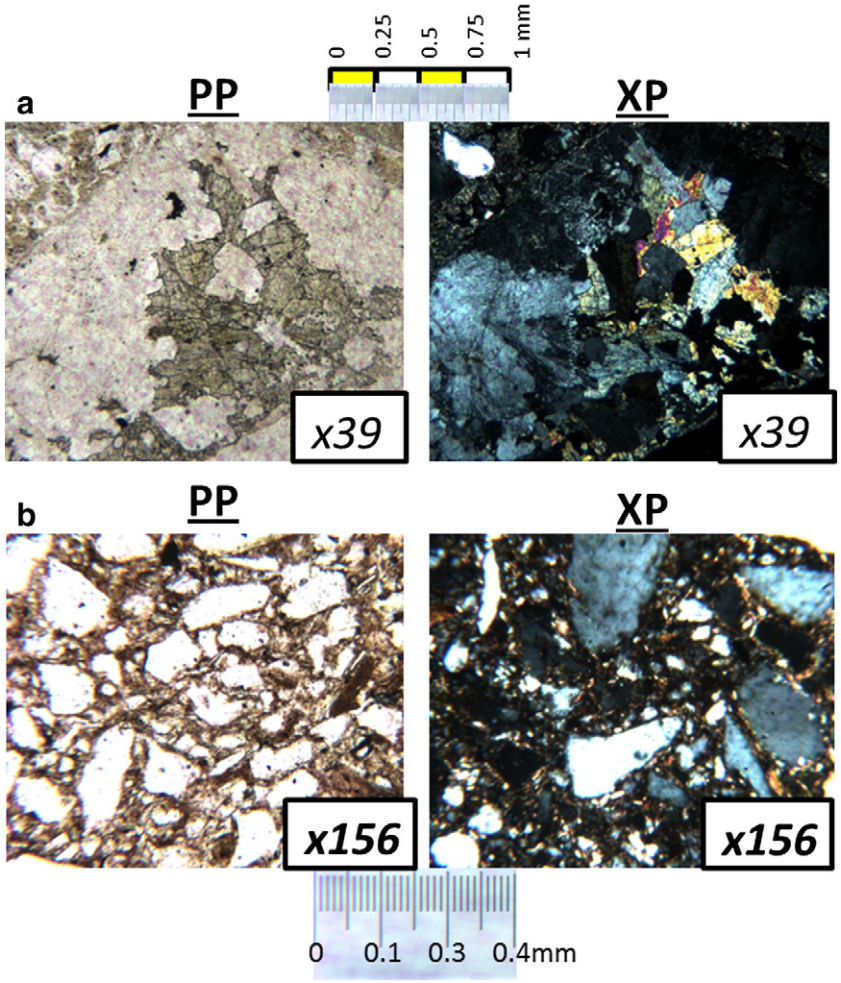


Fig. 2. Photos with a Spot INSIGHT color camera and the SPOT advance software of S01 thin section (B2). PP: plane parallel polarized light. XP: Crossed polarized light. 1 mm ~ 10^{-3} m. a) Low magnification view of carbonate aggregates; b) textural aspect of the quartz micro-conglomerate substratum.

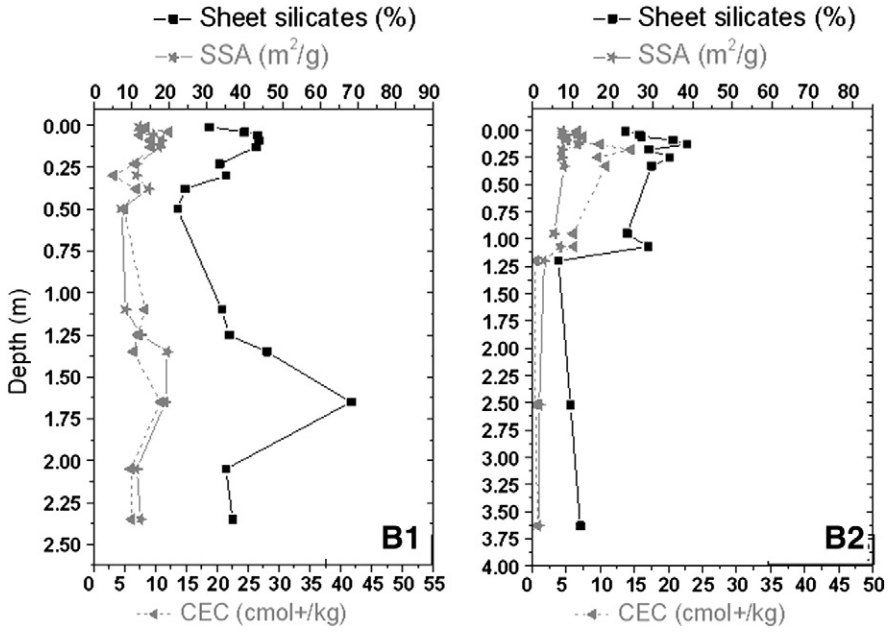


Fig. 3. Sheet silicates, specific surface area (SSA) and cationic exchange capacity (CEC) profiles with depth.

Table 4
Exchangeable cations and cationic-exchange capacity (CEC: $cmol^+\ kg^{-1}$) of the substratum samples.

Sample	B1							B2						
	Exchangeable cations ($cmol^+\ kg^{-1}$)						CEC	Exchangeable cations ($cmol^+\ kg^{-1}$)						CEC
	$NH_4^+{}_{ex}$	$Na^+{}_{ex}$	$K^+{}_{ex}$	$Ca^{2+}{}_{ex}$	$Mg^{2+}{}_{ex}$	$\sum_{ex}$		$NH_4^+{}_{ex}$	$Na^+{}_{ex}$	$K^+{}_{ex}$	$Ca^{2+}{}_{ex}$	$Mg^{2+}{}_{ex}$	$\sum_{ex}$	
S01	0.17	0.07	0.07	0.96	0.41	1.68	8.48	0.24	0.04	0.22	23.34	0.82	24.66	6.62
S02	0.27	0.04	0.07	0.84	0.4	1.62	12.11	0.21	0.03	0.18	13.09	0.65	14.16	6.49
S03	0.2	0.25	0.09	0.75	0.27	1.56	7.44	0.28	0.03	0.16	6.46	0.93	7.86	7.51
S04	0.13	0.21	0.08	0.7	0.3	1.42	9.12	0.29	0.04	0.19	6.32	1.21	8.05	5.12
S05	0.3	0.12	0.12	0.68	0.49	1.71	9.23	0.4	0.06	0.29	8.71	1.55	11.01	9.98
S06	0.61	0.24	0.08	0.66	0.31	1.9	6.71	0.24	0.08	0.13	10.8	1.51	12.76	14.43
S07	0.55	0.12	0.11	n.d.	n.d.	0.78	3.18	0.2	0.05	0.1	8.92	1.38	10.65	9.7
S08	0.28	0.5	0.17	1.12	0.71	2.78	6.86	0.15	0.01	0.09	8.9	1.14	10.29	10.82
S09	0.09	0.03	0.12	1.23	0.75	2.22	4.9	0.03	0.04	0.09	7.11	1.18	8.45	6.03
S10	0.55	0.12	0.12	1.43	0.9	3.12	8.31	0.04	0.03	0.08	9.1	1.04	10.29	6.15
S11	0.02	0.08	0.09	0.44	0.96	1.59	7.17	n.d.	0.02	0.08	0.73	0.14	0.97	0.5
S12	0.03	0.07	0.11	1	1.02	2.23	6.44	n.d.	0.03	0.02	2.2	0.28	2.53	0.49
S13	0.01	0.12	0.11	0.61	1.64	2.49	10.86	n.d.	n.d.	0.01	6.85	0.23	7.09	0.83
S14	0.02	0.07	0.13	1.98	3.61	5.81	6.02							
S15	n.d.	0.11	0.39	2.34	2.13	4.97	6.14							

$\sum_{ex}$: sum of the exchangeable cations $NH_4^+{}_{ex}$, $Na^+{}_{ex}$, $K^+{}_{ex}$, $Ca^{2+}{}_{ex}$, and $Mg^{2+}{}_{ex}$; CEC: cationic-exchange capacity, n.d.: no detected.

by WSOC and the TA–TAC) is inversely related to leachate pH. The basic pH, the low WSOC (at least one order of magnitude lower than other MW landfill leachates) and the higher proportion of TAC than TA–TAC, on the TA, all of them of the leachate (Table 3), indicate that the Cantabria landfill is mainly at some point of the methanogenic stage.

Oxidizing species can be also used as an indicator of the degree of waste stabilization and leachate stage. The degradation by means of redox reactions follows this order chronologically: $O_2 \rightarrow NO_3 \rightarrow MnO_2 \rightarrow Fe(OH)_3 \rightarrow SO_4^{2-} \rightarrow CO_2$, depending on the most oxidizing species present and the availability of microorganisms. The low SO_4^{2-} measured in the leachate denotes the almost complete reduction of SO_4^{2-} to S^{2-}, the last oxidizing compound before the reduction of organic carbon to CH_4. Nevertheless, the above-mentioned high dilution potential of the landfill could jeopardize this aspect. High SO_4^{2-} concentrations belong to aerobic, acetogenic and the beginning of the methanogenic stages (when Eh values are also high). But afterwards, the Eh falls and the SO_4^{2-} decreases due to its consumption by sulphate-reducing bacteria which obtain energy by oxidizing organic compounds while reducing sulphate to hydrogen sulphide (H_2S) during the fermentation (Kjeldsen et al., 2002). This is in concordance with the anaerobic conditions (0.48 mg L^{-1} of dissolved O_2) and with the presumably methanogenic stage of the leachate.

Eh together with pH determine the predominant chemical species of many inorganic compounds, and thus its availability and mobility. The Eh measurements (Table 5) were passed to pe ($pe = -log[e^-] = Eh / 0.059$ at 25 °C and 1 atm) in order to represent pe–pH diagrams and to establish the predominance fields (aquatic species or solid mineral phases) in the substratum samples underneath the landfill. The diagrams show that the predominant Fe species in these samples are the reduced aqueous Fe^{2+} and, to a lesser extent when pHs are basic, the oxidized solid $Fe(OH)_3$. Remaining constant the pe, if the pH decreases, the environment becomes more reducing (Fig. 5). Therefore, the acid environment would explain the hastening of the reducing conditions beneath the methanogenic landfill and the mobility of metals, such as iron.

The measured Eh is close to be regulated by the reduction of iron oxides. Fig. 5 shows, on the one hand, substratum samples with a basic pH (according to the basic pH of the leachate) where the Eh is controlled by the equilibrium Fe^{2+}–Fe $(OH)_{3(s)}$, presenting iron oxides, as it was previously observed in the cements by optical microscopy (Fig. 2b). On the other hand, the substratum samples affected by acidic pH, tend to maintain reducing conditions out of the equilibrium Fe^{2+}–Fe $(OH)_{3(s)}$. All together would be a situation of non-equilibrium in which the reducing leachate is being mixed

Table 5
External specific surface area (SSA: $m^2\ g^{-1}$), pH, redox potential (Eh: mV), electrical conductivity (EC: $mS\ m^{-1}$) and moisture (h: %) of the substratum samples.

Sample	B1					B2				
	SSA ($m^2\ g^{-1}$)	pH	Eh (mV)	EC ($mS\ m^{-1}$)	h (%)	SSA ($m^2\ g^{-1}$)	pH	Eh (mV)	EC ($mS\ m^{-1}$)	h (%)
S01	12	4.9	241	12.1	19.31	7.5	7.4	193	225	22.98
S02	12.5	5	237	9.4	19.01	7.5	6.7	219	84.6	22.73
S03	15.5	4.7	253	10.1	20.14	8	6.7	201	48.1	24.97
S04	18	4.7	258	9.1	20.87	8.5	6.6	182	28.8	26.78
S05	17.5	4.8	267	8.8	18.87	11.5	6.3	169	27.1	35.69
S06	11.5	5	233	11.1	20.1	7.5	6.2	173	41.5	43.35
S07	11.5	5.1	232	9.7	16.93	7.5	6.1	176	40.1	37.02
S08	14.5	5.5	245	11.2	16.17	8	5.9	182	53.6	34.23
S09	7.5	5.8	233	26.2	18.33	5.5	5.9	167	15.6	25.94
S10	8.5	5.1	228	17.4	24.56	7	6.5	171	26.7	27.58
S11	12.5	4.5	350	19.6	14.88	3	7.5	145	3.8	9.55
S12	19.5	4.5	323	13.8	19.72	1.75	8.8	128	6.9	10
S13	19	4.4	325	14.2	17.17	1.55	9	113	6.2	9.69
S14	11.5	5.2	300	5.2	12.07					
S15	12.5	5.6	290	4.8	11.58					

Table 6
Water soluble organic carbon (WSOC, μg g^{-1}) and soluble ions (mmol kg^{-1}) of the substratum samples (aqueous extracts).

Sample	B1							B2							
	WSOC	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	WSOC	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	Alk
	(μg g^{-1})	(mmol kg^{-1})						(μg g^{-1})	(mmol kg^{-1})						
S01	240	0.95	3.79	6.28	1.17	n.d.	0.15	185	2.74	3.59	1.92	81.36	3.11	n.d.	16.78
S02	252	1.16	3.73	3.62	n.d.	n.d.	1.35	115	3.12	1.77	1.5	49.07	2.44	0.17	9
S03	167	0.76	4.86	4.79	n.d.	0.84	0.26	124	3.23	2.89	2.83	7.03	0.45	0.5	1.92
S04	136	0.64	2.23	1.99	n.d.	n.d.	0.26	127	3.42	2.79	3.84	4.68	0.66	1.11	1.22
S05	96	0.5	2.42	0.94	n.d.	n.d.	0.18	195	3.34	4.54	5.89	5.54	0.42	1.2	4.46
S06	392	2.41	2.22	5.35	2.1	n.d.	0.29	186	3.03	4.99	2.33	11.97	1.42	0.5	4.68
S07	384	2.31	3.6	4.39	n.d.	n.d.	0.18	165	4.25	3.78	1.71	5.93	0.57	0.45	n.d.
S08	45	0.36	2.9	0.54	n.d.	0.66	n.d.	151	1.94	3.52	1.47	10.84	0.9	0.21	n.d.
S09	48	n.d.	0.91	0.67	n.d.	1.62	n.d.	132	0.27	2.46	1.86	3.8	0.31	0.95	2.05
S10	417	2.66	7.63	5.39	2.71	n.d.	0.15	96	0.49	1.77	1.28	16.66	1.62	0.37	3.4
S11	34	n.d.	0.64	0.41	n.d.	0.71	1.24	44	n.d.	0.96	0.22	1.85	0.44	0.87	1.92
S12	30	n.d.	1.33	0.63	n.d.	1.08	1.13	106	n.d.	0.91	0.6	2.46	0.41	1.11	2.49
S13	34	n.d.	1.04	0.61	n.d.	0.96	1.1	118	n.d.	0.71	0.6	3.03	0.5	1.03	2.64
S14	62	n.d.	3.85	1	n.d.	n.d.	1.02								
S15	103	n.d.	2.29	3.45	1.58	n.d.	0.95								

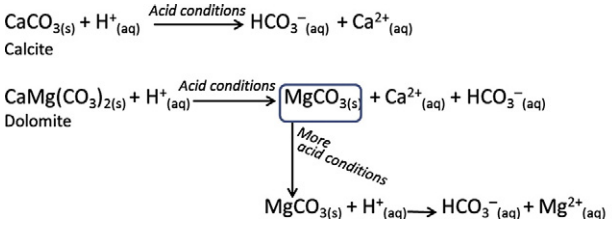
SO_4^{2-} was not detected, Alk: alkalinity (B1 presented no alkalinity), n.d.: no detected.

with a previously altered substratum, under oxidizing and acidic conditions. The high rainfall in the area would favor this situation as it increases drainage and prevents stagnant conditions.

4.2. Leachate effect and soil response

The interaction between the leachate and the substratum depends on leachate composition (Table 3). The low soluble salt content in the substratum samples (even Na^+, NH_4^+, K^+, Cl^- or the alkalinity; the most abundant ions in the leachate) and the predominance of divalent cations in the exchange complex (Tables 6 and 4) suggest that the substratum had not enough retention capacity for leachate pollutants. This is accentuated in the case of B1, because EC values are smaller (12 ± 6 mS m^{-1}) than in B2 (47 ± 58 mS m^{-1}) and because the main leachate components did not follow a declining trend with depth, unlike B2. On the whole, this denotes a quicker leakage of pollutants through B1 than through B2.

Clays are the natural materials with the highest ability to retard the transport of liquids and soluble ions because of their small particle size, high micro–mesoporosity, elevated compaction and a high surface charge (Warith and Yong, 1991; Batchelder et al., 1998; Yong et al., 1999; Hermanns Stengele and Plötze, 2000; Joseph et al., 2003; Chen et al., 2005). This results in a low hydraulic conductivity and the recognition that the filtration decreases as clay content increases (Shevnin et al., 2006). In spite of this, B1 (rising to over 40 mass % sheet silicates in some samples) did not show a significant retention of the main leachate components as other materials with similar soil characteristics did (Regadío et al., 2012), while B2 (with a sheet-silicate content lower than B1) presented a mild retention



(4)

of solutes in the first 1.2-m depth (Fig. 6 right). The generally irregular shape of the measured chemical profiles (Fig. 6) is consistent with the rainy climate and the non-equilibrium redox situation previously discussed.

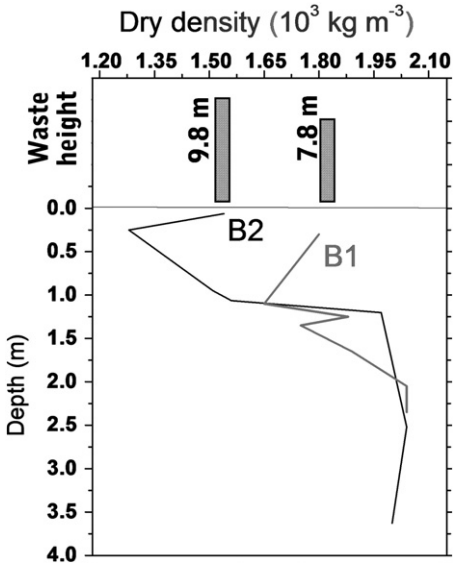


Fig. 4. Waste heights and evolution of dry density (δ) with depth by boreholes.

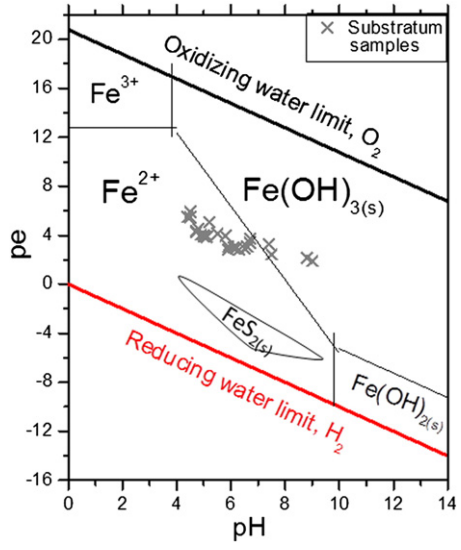


Fig. 5. pe–pH diagram for the system Fe–O_2–H_2O (25 °C and 1 atm). (s): solid mineral phases.

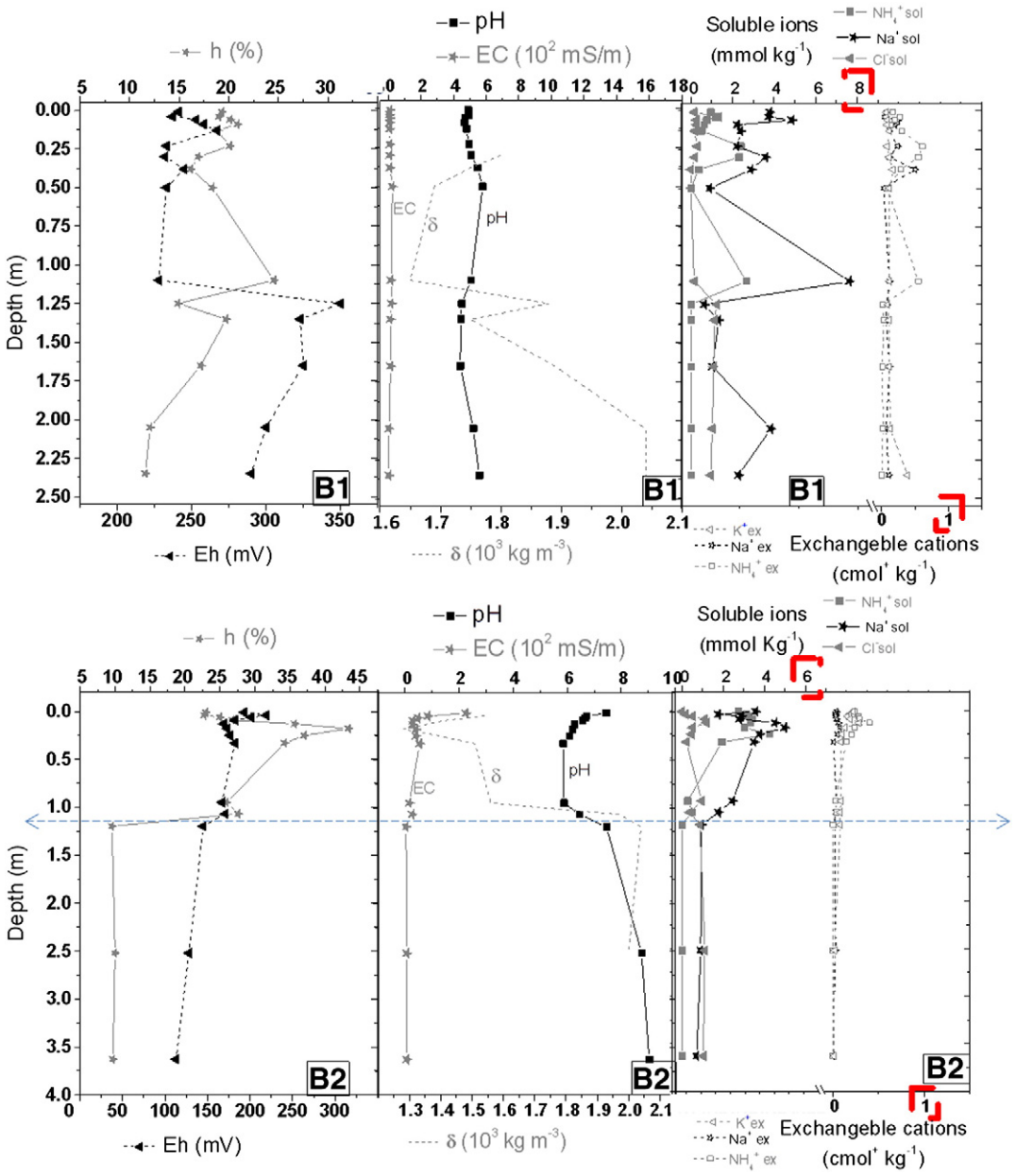


Fig. 6. Evolution of moisture, h; redox potential, Eh (left); pH, electrical conductivity, EC; dry density, δ (center), soluble ions and exchangeable cations (right) with depth in B1 (up) and B2 (down). <————>: depth extent of some retention of the pollution front.

Two differences, that may explain the different barrier behaviors between both boreholes, were distinguished. On the one hand, the not as acid pH in samples from B2 as in those from B1 (Table 5) and on the other hand, the kind of sheet-silicate minerals analyzed in the substratum profiles.

Leachate pH is >7 (Table 3), however the average pH in the substratum is <7 (Table 5). The fact that the leachate has an alkaline pH and that leachate pH increases with time in the methanogenic stage leads to the belief that there was an acid discharge (punctual or discontinuous) that affected more B1 than B2 samples. The consequences of the acidity were the possibility of dissolution of minerals, including illite minerals to form kaolinite (Rosenberg and Kittrick, 1990) and the provision of H^+ and $Al(OH)_3^{x+}{}_{-x}$.

It was showed above how acidity, at the corresponding Eh, drives to the dissolution of iron oxides, releasing Fe^{2+} to the solution, thus becoming mobile and available. The possible dissolution of minerals (carbonates or hydroxides) bound to metals is expected to be high due to the pH values determined in the substratum samples (Table 5). A previous natural presence of carbonates in the substratum could explain the dominance of $Ca^{2+}{}_{ex}$ and $Mg^{2+}{}_{ex}$ over the other exchangeable cations (Table 4), as it is not feasible to come from the leachate (where both cations are in much less concentration than Na^+, NH_4^+ or K^+). Carbonates are easy to dissolve at slightly acidic pH (Eq. (4)), releasing Ca^{2+} and HCO_3^- and, in some cases, Mg^{2+} to the solution.

In the case of dolomite minerals, the rich-Ca^{2+} portion is dissolved before the rich-Mg^{2+} one (Sherman and Barak, 2000). When the former is completely dissolved, more and more Mg^{2+} begins to be released. The ratio $Ca^{2+}{}_{ex}/Mg^{2+}{}_{ex}$ is much smaller in B1 than in B2, denoting the pre-existence of dolomitic carbonates and the further dissolution stage in B1 than in B2. Unlike B1, in B2 the dissolution of dolomitic carbonates was not completed.

Dissolution of minerals decreases density, increases the porosity and, consequently, the hydraulic conductivity; i.e., the ability to

Table 7
Illite and kaolinite content and ratio at different depths in B1 and B2.

Sample depth (m)	B1			Sample depth (m)	B2		
	Illite (%)	Kaolinite (%)	Ill/Kln		Illite (%)	Kaolinite (%)	Ill/Kln
0.01	11	20	0.6	0.01	12	11	1.1
0.04	16	24	0.7	0.06	14	13	1.1
0.09	17	27	0.6	0.18	17	12	1.4
0.38	9	15	0.6	1.07	11	18	0.6
1.65	36	32	1.1	2.52	4	6	0.7
2.35	27	10	2.7				

transmit water, which would reduce the retention capacity of the substratum. It releases cations, too; commonly Ca^{2+}, Mg^{2+}, Fe^{2+}, Mn^{2+}; but heavy metals were also seen to be released under acidic conditions (Wong et al., 2007). These facts may have happened in B1 substratum as attenuation profiles were not observed.

On the other hand, kaolinite formation is enhanced in acid environments. This mineral usually forms in hydrothermal acid solutions or in high weathering rate regimes under warm, rainy climate conditions (as Atlantic climate), by alteration of a rich aluminium lithology (Eq. (5)), typical from products of weathered rocks, which were originally rich in feldspar (Hua et al., 2007). In this respect, some alteration of illite or feldspar (rich aluminium minerals identified in the XRD patterns) could turn them into kaolinite, in the long term.

$$\underset{\text{Metamorphic/ igneous feldspars}}{2KAlSi_3O_8 + 11H_2O} \xrightarrow{\textit{Hydrolysis}} \underset{\text{Kaolinite}}{Al_2Si_2O_5(OH)_4} + 4H_4SiO_4 + 2K^+ + 2OH^- \quad (5)$$

This is illustrated by the illite/kaolinite ratio (Table 7): this ratio is smaller in B1 (no retention) than in B2 (some retention); and within B1, it is smaller in the closest samples to the leachate source (increasing with depth). The low values at depths >1 m in B2 may be explained by some lateral migration of the presumed acid discharge.

Both clays kaolinite and illite are sheet silicates; i.e., minerals constituted by the repetition of alumino-silicate sheets. The main difference between both is the charge and therefore the ionic exchange capacity (normally the CEC). Kaolinite and illite have a *variable charge* in the lateral broken edges or boundaries of the sheets (external surface), which is affected by, and varies with, changes in pH: at alkaline pH, cations are adsorbed in the broken edges and at acid pH, anions are adsorbed (Fig. 7). Unlike kaolinite, illite has a not neutral internal structure (within sheets) that constitutes a *negative permanent charge* (internal surface). This permanent charge is neutralized by cations (mainly K^+, which is irreversibly adsorbed) that enter in the interlaminar positions (Brigatti et al., 2006) increasing the interlaminar space and the cohesion within illite sheets due to the ionic bonds between K^+ and the permanent negative charged layer. Kaolinite sheets are neutral and more weakly joined by van der Waals forces (Fig. 7). As a consequence, kaolinite has less CEC than illite, which exhibits both inter-crystallite and edge charged surfaces.

Surface reactions (such as the CEC) have been extensively claimed to prevent pollutant transport through clayey substrata (Sawhney, 1996; Bradl, 2004; Goldberg et al., 2007; Galvao et al., 2008), which denotes the preference for illite rather than kaolinite as a pollution barrier. Furthermore, the acid pH also affects the *pH-dependent charge*, transforming the sheet-silicate minerals into anionic exchangers. An anionic exchanger is not as desirable as a cationic one because the main inorganic pollutants in the leachates, e.g., heavy metals; are positively charged (Table 3).

Finally, the H^+ and $Al(OH)_3^{x+}{}_{-x}$ that come from an acidic emission could react with the alkalinity components. This would explain the null neutralizing capacity of B1 samples (Table 6), though being alkalinity one of the major components in the leachate (Table 3) and though the possible dissolution of carbonate minerals that would release alkalinity components (Eq. (4)). Once the alkalinity components have been depleted, the rest of H^+ and $Al(OH)_3^{x+}{}_{-x}$ may have replaced the cations naturally present in the exchangeable complex. The fact that the sum of the exchangeable cations measured (NH_4^+, Na^+, K^+, Ca^{2+} and Mg^{2+}) resulted in most of the cases lower than the CEC measurements (Table 4) could be caused by the presence of H^+ and $Al(OH)_3^{x+}{}_{-x}$ in the exchangeable sites. This, together with the presumable transformation of illite into kaolinite structures under acidic conditions, decreases the CEC and hence, the retention of cationic pollutants dissolved in the leachate.

Thus the retention capacity seems to depend not only on clay content, but also on the exposure conditions (acidity) and the resulting kind of clay (kaolinite, illite…). The data showed lower SSA and sheet-silicate content but higher CEC in B2 than in B1, which proves that a reliable indicator of the barrier capacity of a substratum is the CEC, better than the external surface or the sheet-silicate quantity. This is because the CEC reflects the total charge (permanent and variable) at neutral pH, while the SSA may be related to available positions in which the pH-dependent charge can be developed, and because different sheet silicates have different retention properties.

The mild retention of the ions in the first 1.2 m of B2 (Fig. 6 down right) is according to the decrease of the h, the Eh and the EC (Fig. 6 down left and center) and to the increase of the pH >7 and the δ (Fig. 6 down center) below the 1.2-m depth. High pH promotes the precipitation of soluble compounds (Ca^{2+}, Mg^{2+}, Fe^{2+}, Mn^{2+}, heavy metals) as sulphides, hydroxides or carbonates, decreasing their concentration in the leachate (Harmsen, 1983). Low Eh enhances sulphide precipitation in anoxic conditions (Taylor and Allen, 2006). Finally, high density reduces the channels through which liquids move and, therefore, the h. This is in concordance

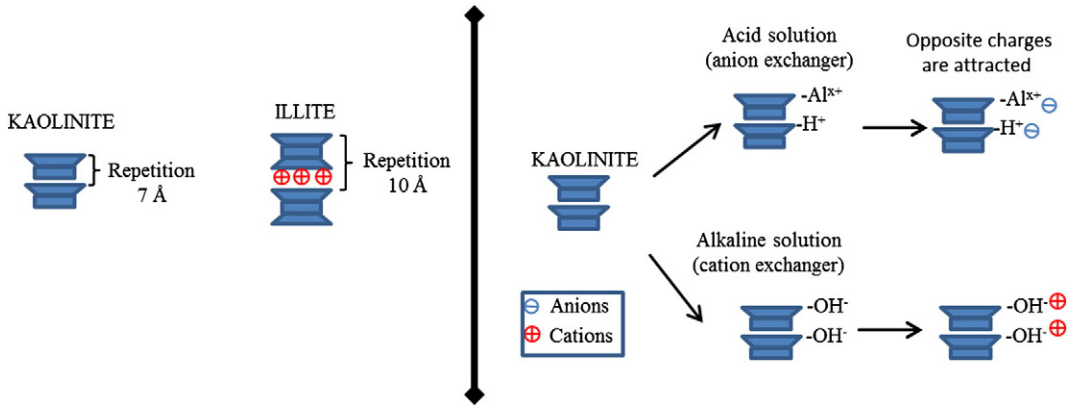


Fig. 7. Left: Kaolinite and illite structures. Right: Representation of kaolinite pH-dependent charge: anion exchanger and cation exchanger.

with the dissolution of minerals under acidic conditions in the shallow samples, which would decrease the density.

Marzougui and Ben Mammou (2006) analyzed boreholes, under a landfill, of a substratum (30–45 mass % of sheet silicates composed of kaolinite and minor illite and smectite) similar to that of this study. They recorded retention depths as long as 3 m for COD. These depths are longer than the minimum thickness required to accept a natural substratum as a geological natural barrier of a landfill, with a maximum hydraulic conductivity of 10^{-9} m s^{-1}, established by the Directive 1999/31/EC (1999). Warith and Yong (1991) also observed the undesirable retention qualities of acidity and kaolinitic materials. In this case, a leaching experiment through a kaolinite column associated with an acidic environment resulted in a higher motion of some cations in the leachate solution, compared to an illite column and to a natural clay column, the latter with a CEC (60 $cmol^{+}$ kg^{-1}) typical of illite/smectite materials.

To summarize, under acidic conditions some minerals are dissolved (due to the supply of H^{+} and the enhancement of reducing species), decreasing the density (and, thus, increasing the porosity and the hydraulic conductivity) and releasing cations and other metals which may become a new pollution source. In addition, the acidity decreases the available CEC of the substratum (an essential mechanism for retaining the solution pollutants) through three ways: (1) acid environments favor the transformation of illite into kaolinite (lower CEC), in the presence of rain, (2) as pH decreases, the CEC of the mineral decreases to the point that when pH is <7, the CEC disappears at the expense of the anionic exchange capacity, and (3) H^{+} and $Al(OH)_3^{x+}{}_x$ can end up with the neutralizing capacity of the substratum (necessary to buffer the pH) and occupy the exchangeable sites, decreasing the number of available positions for retaining cationic pollutants.

To combat any of these effects and to ensure a safe landfill practice, it is proposed to avoid acid wastes and, when not possible, to select clay substrata containing carbonates as accessory minerals. Any clayey substratum has a limited pH-buffering capacity. The presented measure would provide the substratum of buffer capacity and resilience to face potential acid spills and the ability to assimilate the acid cations by the HCO_3^{-} that have been added.

5. Conclusions

A precise control of processes in the leachate–substratum interaction is necessary to avoid or treat a predictable pollution in existing landfills and to ensure safe barriers in those to be built in the future. This study analyzed substratum samples from boreholes B1 and B2 under a 9-year old landfill. The actual pollution source was a methanogenic leachate with a basic pH and important concentrations of Na^{+}, NH_4^{+}, K^{+}, Cl^{-}, alkalinity and organic compounds. The clayey substratum presented an acid pH and low levels of soluble and exchangeable ions, primarily divalent ions, without a recognizable attenuation trend as a function of depth. These characteristics indicated that leachate pollution passed through the natural clayey material without being retained by it. Only in B2, a small part of the pollution was immobilized in the first 1.2 m of the substratum.

The study evidenced that a natural clayey substratum cannot retain the leachate pollution when an unprecedented acid discharge occurs and the kind of sheet silicates present in the material has an important pH-dependent charge compared to the negative permanent one. The main factors that explained the mobilization and development of pollution under this landfill were the increase of hydraulic conductivity and decrease of dry density, the release to the solution of cations fixed in solid phases and the decrease of the CEC; the latter being responsible for the retention of cationic pollutants in the solution.

The threat of leachate pollution posed here suggests that care should be given to the disposal of acidic waste in old and future landfill sites, preventing acid disposal and ensuring a neutralizing capacity of the substratum. In the case of new landfills, it is important to choose a proper substratum as a natural geological barrier to retain leachate components. This barrier can be described as a clay material with sufficiently high, and not pH-dependent, CEC.

Acknowledgments

This work was supported by the Spanish Environmental Ministry (MMA: I+D+i A113/2007/3_02.6) in cooperation with Geotecnia y Cimientos S.A. (GEOCISA) and Centro de Experimentación de Obras Públicas (CEDEX).

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